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PROCESS AND DEVICE FOR PLASMA SURFACE TREATMENT

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Process and Device for Plasma Surface Treatment

The present invention concerns a process for plasma surface treatment and a device for realization of the process. The treatment can be deposition of a barrier film, sterilization, cleaning, etching, or creation of a surface alloy.

In the current state of the art, plasma depositions in a vacuum and at atmospheric pressure are proposed. The vacuum technologies provide for a uniform treatment of complex surfaces such as the inner surface of a PET bottle, but they are slow and relatively expensive, since it is necessary to create, and work in, a vacuum chamber. The corresponding equipment is complex, extremely costly, and difficult to adapt to different types of container. The requirement that the equipment be perfectly sealed is very difficult to satisfy and has repercussions on the reliability of the process and uniformity of the results.

Processes working with plasmas at atmospheric pressure have been discussed in several publications, for instance patent GB 1,098,693, patent application WO 97/22369, and patent application WO 99/46964.

In patent GB 1,098,693, a device for treatment of the inner surface of a plastic bottle designed to sterilize this surface is described. The device comprises a central electrode introduced into the bottle and an external electrode surrounding the bottle, the two electrodes forming a coaxial system connected to a high-frequency current source. Argon (Ar) is introduced into the bottle through a hole in the central electrode in order to reduce the electric potential needed to create the plasma. The device described in this patent is characterized by a high electric field, of the order of 450 V/cm, and a very weak current, of the order of a few milliamperes. The treatment time is too long and the power too low for this process to find industrial application and to be able to compete with the vacuum plasma techniques.

In patent application WO 97/22369 concerning the sterilization of plastic containers, it is proposed to form a plasma with a source of RF current providing a high-amplitude current. It is proposed, moreover, to take the central electrode out of the bottle, which permits a rhythm of PET bottle sterilization in line with industrial needs. A disadvantage of the process and of the device described in the aforementioned application is that a uniform treatment of the surface to be treated is obtained. It is to be expected that the plasma covers only part of this surface. This results in poor sterilization of surface parts that have not been in contact with the plasma. For the same reasons such a process would not be able to provide a uniform barrier over the whole inside surface of a container.

In patent application WO 99/46964, a surface treatment process is described where a pulsed plasma cord is formed at atmospheric pressure which sweeps the surface to be treated by relative motion of this surface and the device producing and defining the plasma cord. One might expect that such a process would be able to yield a layer that is impermeabilizing, for instance, or could uniformly sterilize the surface to be treated, since the plasma cord sweeps all of the surface to be treated. In reality it is found to be difficult to obtain a surface treatment, and more particularly the deposition of a film or a sterilization of satisfactory quality.

For reasons of local heating the plasma column must be moved relative to the surface to be treated. The velocity dictated by the need not to overheat the material of the surface to be treated is higher than the optimum speed of treatment in many applications. One of the consequences consists in the fact that a boundary layer of cold gas drawn along by the object blows into the discharge and moves it away from the surface to be treated. This removal lowers the diffusive flux of active plasma particles toward the surface to be treated. This problem can be resolved in part by renewing the discharge by pulses.

However, the pulse frequency is also dictated by the need not to overheat the material of the surface to be treated, and hence cannot be optimized for different applications.

The volume of plasma created by known processes for atmospheric plasma treatment is large and leads to poor yields, since large part of the energy input is lost for heating the surrounding gas and the object to be treated. For applications involving the deposition of barrier films, on the other hand, powder forms in the bulk of the plasma string (SiO_2 powder, for instance) and deposits on the surface to be treated. This powder, which adheres but weakly to the surface, represents an obstacle to the creation of high-quality films.

The disadvantages and limitations of known plasma treatment processes are not limited to the points described above. For example, in the case of plasmas close to a thermodynamic equilibrium state, such as would arise from the process described in WO 99/46964, it is difficult to perform an electron bombardment of the surface to be treated, since in general the mean path of the electrons ($\leq 10^{-4}$ cm) relative to the elastic interactions of the surface to be treated is shorter than the thickness of the plasma boundary layer ($\geq 10^{-2}$ cm). It follows that it is difficult for such a process to adapt the substrate/film interface to a desired quality of treatment, for instance by activating the surface to be treated prior to film deposition so as to ensure good adhesion. It follows that it would be equally difficult to produce films consisting of several layers differing in their composition, with each layer being activated prior to deposition of the following layer.

Experience shows that despite the relative motion of the plasma and object to be treated in known processes, local overheating is inevitable and provokes breakdowns that give rise to defects and local destruction of the surface to be treated. This disadvantage is particularly important in certain applications, as will be explained by way of example hereinafter.

Polymerizable materials such as PET (polylethyleneterephthalate), PE (polyethylene), PP (polypropylene) and others are used in various industries for products such as containers for beverages and food, the pharmaceutical and perfume bottles and tubes, gasoline tanks, containers for chemical products, as well as the neon tubes for night-time advertizing, particularly for reasons of low cost and weight of these materials. Yet one of the disadvantages of polymeric materials is their gas permeability. The permeability of the PET bottles used in the food industry, for instance, lets oxygen diffuse through the bottle wall and oxidize the food or beverages, which for this reason progressively lose their properties such as their taste, odor or color. Carbonated beverages to the contrary lose their carbon dioxide. Excessive plastic container permeability shortens the time of conservation of the foods. Gas diffusion across the plastic walls can have ill effects on large number of other products such as pharmaceuticals, cosmetics, hygiene and housekeeping products. In the case of gasoline tanks or other containers holding chemicals, the permeability of the plastic materials allows these chemicals to penetrate into the plastic material so that this can no longer be recycled easily and may present a fire hazard. The permeability of plastics implies that neon tubes in plastic have a lifetime too short to be marketable.

Another problem of plastic materials arises from aromatic molecules such as acetaldehyde forming in the bulk material and then diffusing toward the surface where they enter the liquid held by the container. Such molecules alter the taste and odor of the beverage or food item.

One solution consists in coating the inside of the container by an impermeable film called "barrier". Different compositions such as carbon, aluminum oxide, and silicon oxide (SiO_2) can form barriers on polymers. The deposition of a barrier film can be carried out by plasma in contact with the surface, and in the presence of a gas furnishing the molecules that will form the layer. However, the plastic materials mentioned above

do not withstand temperatures above around 60 to 70 °C, so that it is difficult with the known plasma treatment processes to avoid local overheating or obtain a sufficiently high quality of the treatment. For instance, the barrier films deposited on PET bottles by traditional industrial plasma treatment processes yield a factor (RIF) of impermeability enhancement relative to the untreated material that is of the order of 20 to 30 for oxygen or 5 to 6 for CO_2. Typical defects of such barrier layers are lack of adhesion and flexibility and the appearance of cracks leading to a loss of impermeability. These defects may also represent a hazard for the consumer.

Many other materials do not withstand the temperature rise that would be required for optimizing the plasma surface treatment process. This is the case, for instance, with the silicon wafers used in semiconductor industry. The semiconducting structures at the surface of the circuits can in fact be altered or damaged by high treatment temperatures because of an accelerated particle diffusion across the interfaces of the different layers deposited on the silicon wafer.

Considering the above, it is an object of the present invention to provide a plasma surface treatment process that is performant and reliable in an industrial environment, as well as a device for performing a plasma surface treatment process that is performant and reliable in an industrial environment.

It is a further object to provide a plasma surface treatment process as well as a device for realizing the process that can be used to treat the surfaces of materials that are sensitive to high temperatures.

It is a further object of the invention to be able to deposit a barrier on containers (particularly plastic containers such as PET bottles in the food industry, polyethylene tubes in perfumery, and gasoline tanks in the automobile) that is strong, flexible and has a good impermeability. It would be advantageous to be able to simultaneously treat the

inner and outer surfaces of hollow objects (bottles, tubes, tanks). It is advantageous to be able to treat the surface of a complex object.

It is another object of the invention to provide a plasma surface treatment process as well as a device for realizing the process that can be used to deposit several layers of different materials on a surface to be treated.

It is also advantageous to be able to perform other surface treatments such as cleaning, etching, surface activation, sterilization or the formation of surface alloys.

It would also be advantageous in many applications, moreover, to realize a process of plasma surface treatment at atmospheric pressure as well as a device for realizing the process.

Objects of the invention are achieved by a process according to claim 1.

In the present invention, a process for plasma treatment of an object's surface to be treated comprises the creation of a plasma, the application of the plasma to the surface to be treated, and the excitation of the surface to be treated, such that it undulates. The energy for excitation of the surface may come from the process creating the plasma, from an external source, or from a combination of these two sources. The vibration of the surface to be treated preferably takes place while the plasma is being applied to the surface to be treated, but depending on the treatment to carry out, it may also take place just prior to and/or just after the application phase.

The energy for excitation of the surface that comes from the plasma creation process may advantageously come from a shock wave developing at the plasma front during its creation. The shock wave is created by providing that the front of plasma development creates within the plasma a pressure such that its ratio to the ambient pressure be above

the critical value for formation of a shock wave in the given gaseous medium. This is obtained by selection and control of the plasma generation parameters, particularly the energy density and the lifetime of the plasma development front.

The energy for surface excitation coming from an external source can come from a vibration generator in contact with the object to be treated, or not in direct contact with the object to be treated by way of acoustic waves, for instance ultrasonic waves. For many applications and many objects to be treated, the vibration frequency will advantageously be within the range of ultrasonic frequencies. The external generator can also furnish energy in the form of shock waves.

The vibration of the surface to be treated can be the result of excitation of one or several eigenfrequencies and their harmonics associated with the body of the object to be treated, by an abrupt leap of energy (shock) and/or by the action of an external generator emitting one of several frequencies close to or identical with eigenfrequencies or their harmonics associated with the object to be treated. The vibration of the surface to be treated can also result from forced frequencies when an external generator emits frequencies that are not harmonics of the eigenfrequencies of the object to be treated.

For most applications the plasma is preferably created with an electrical or electro-magnetic energy source operated continuously, by unipolar or alternating pulses, or at high frequency. This may for instance be a discharge of the capacitive or inductive type, or high-frequency waves. However, the plasma can also be created by adiabatic compression or by shock waves, furnished for instance by an adiabatic-compression or shock-wave generator.

The plasma created by a surface treatment process according to advantageous embodiments of the invention may be in thermodynamic disequilibrium for large part of the plasma's lifetime.

The process according to the invention is very advantageous, since it permits utilization of a cold plasma while intensifying the interaction of the plasma with the surface to be treated, and hence to optimize the plasma surface treatments for a large range of applications, including treatments of objects consisting of materials withstanding only a very slight temperature increase, such as PET and semiconductors. The undulation of the atoms and molecules of the surface to be treated actually intensifies the effect of the activated plasma particles on the surface to be treated. Because of the intensified effect, one has a larger choice of plasma generation modes (adiabatic compression, shock waves, electrical discharge) and can optimize the process depending on the features (material, shape, dimensions) of the object to be treated and treatment to be performed. It is possible in particular to use a "cold" atmospheric plasma (as defined by R. F. Baddour and R. S. Timmins in "The Applications of Plasmas to Chemical Process", MIT Press, page 17), that is, out of thermodynamic equilibrium, so that the insulating surface to be treated remains cold while electrons can bombard the surface to activate it. This plasma can for instance consist of a network of filaments that appear, move along the surface, and disappear within times sufficiently short to not heat up the surface to be treated.

The process according to the invention, on the one hand, accelerates surface treatment by ionizing and activating plasma particles with the aid of shock waves resulting from the filament branches of the plasma discharge when the shock waves are reflected by the surface to be treated, and on the other hand, intensifies the surface treatment without any important increase in temperature of the object to be treated, since the vibrations of the surface to be treated influence the interaction of the surface with the plasma, in a similar manner to the atomic agitation produced by an increase in temperature of the object.

The surface treatment can be further intensified by adding the vibrations of an external acoustic frequency or ultrasound generator, preferably adjusted so as to amplify the

eigenfrequencies of the object to be treated. The improved interaction of the plasma with the surface to be treated at low temperature has many other advantageous consequences. For instance, composite films of good quality can be obtained by the successive deposition of layers that adhere well to the substrate and have different physical, physicochemical, and mechanical properties.

Another advantage of the process according to the invention is that it enables treatment of the inner walls of a complex object lacking axes of symmetry, such as a gasoline tank.

A device of plasma surface treatment according to the invention may advantageously comprise an external acoustic vibration generator.

A device of plasma surface treatment according to the invention may advantageously comprise a vibration sensor. The vibration sensor allows one to verify and/or analyze the eigenfrequencies of the object to be treated, in order to adjust the device, for instance the parameters of the electrical discharge generation circuit for plasma creation, for the production of shock waves which will produce vibration of the surface to be treated of a specific object to be treated, or for verifying the satisfactory functioning of the process and particularly the quality of the vibrations of the surface to be treated in an industrial process. Variations in the expected frequency and amplitude spectra would provide information on a possible failure or quality reduction of the surface treatment being carried out.

A plasma surface treatment device according to the invention may advantageously comprise one or several live electrodes provided with one or several process gas supply ducts for generation of one or several plasma jets by electrical discharge. The live electrode may advantageously rotate, so that it will be able to move the plasma or plasmas by electrostatic and hydrodynamic effects along the surface to be treated.

The device may comprise a live electrode that is in the form of a liquid jet that is movable relative to the object to be treated in order to project a conducting liquid jet against a wall of the object to be treated so that a plasma is created on the other side of the wall.

According to an embodiment of the invention, the electrodes for plasma generation by electrical discharge can be connected to the opposite poles of an electrical circuit. These electrodes can be utilized to generate a plasma on both sides of a wall of an object to be treated, the fluxes of the plasma being anti-parallel on the two sides.

One can also furnish a device with at least two live electrodes in order to treat respective sides of one wall of an object to be treated, the plasma fluxes on the two sides being parallel and directed toward a grounding electrode.

A plasma surface treatment device according to the invention may advantageously comprise a liquid bath into which the objects to be treated, particularly containers, are immersed while plasma is applied to the inner surface to be treated. This may for instance be bottles or other containers partly immersed into the liquid bath, with their neck remaining above the surface of the liquid. The liquid is thus in contact with the outside of the container, which offers the advantage that the container wall can be cooled very efficiently and the plasma applied for a longer time. When an external source of vibrations is used, then the liquid will on the other hand serve to make the vibrations more uniform across the container wall, and thus on the container's inner surface to be treated.

A plasma surface treatment device according to the invention can advantageously comprise a system of surface quality control after or during the treatment with a laser beam recording, either the number of photons emitted by non-linear effects during

passage of the laser beam across the surface treated, or the decrease of the flux of primary protons due to their recombination resulting from non-linear effects, the laser beam system being provided with a device for the detection and analysis of the beam reflected from the surface to be treated or traversing the surface to the treated.

A plasma surface treatment device according to the invention may comprise an enclosure in which the objects to be treated are arranged, and a piston for compressing the process gas in the section of the enclosure where the objects to be treated are arranged, so as to create a plasma by adiabatic compression. The piston can be driven by a device with compressed air or other gases located in the section of the enclosure above the piston.

A plasma surface treatment device according to the invention may advantageously comprise an enclosure with one section where the objects to be treated are arranged, and with another section where a process gas is kept under pressure and which is separated from the other section by a wall that can be removed or destroyed in order to permit instant decompression of the compressed gas for the purposes of creating a shock wave that moves in the direction of the objects to be treated.

Other advantageous aspects of the invention will become apparent from the claims, from the following description and from the attached drawings in which:

Figures 1a and 1b are simplified schematic illustrations of devices for the treatment of surfaces of objects to be treated, according to the invention;

Figures 2a and 2b are electron-microscope (SEM) surface photographs of the treated surface of a PET bottle with a silicon-oxide-based barrier;

Figure 2c is a SEM photograph of the treated surface of a PET bottle with a silicon-oxide-based barrier obtained by an atmospheric plasma deposition process according to the invention;

Figures 3a and 3c are simplified perspective views of devices for plasma surface treatment according to embodiments of the invention, in these particular cases for the treatment of inner walls of bottles;

Figures 4a and 4b are high-speed photographs of PET bottles obtained during their plasma surface treatment according to the invention, where the treatment of Fig. 4a uses a process gas prepared from a mixture of hexamethyldisiloxane, oxygen, and argon, and the treatment of Fig. 4b uses argon alone as a process gas;

Figure 5 illustrates plots of voltage U and current I as functions of time for a plasma generated by electrical pulse discharges according to the invention, either in a unipolar mode (plots A1 and A2) or in a high-frequency mode (plot B);

Figure 6 is a sectional view across part of the wall of an object to be treated during a plasma treatment according to the invention;

Figure 7 is a view of an oscilloscope screen connected to a vibration sensor measuring the vibrations of an object to be treated during a plasma treatment according to the invention, here of an 0.5-liter PET bottle during treatment by an electrical pulse discharge with the aid of a high-frequency generator producing a branched network of plasma filaments according to the invention;

Figure 8 is a simplified sectional view of a plasma surface treatment device for a container of complex shape according to the invention;

Figure 9 is a simplified sectional view of another embodiment of a device for plasma treatment of a container of complex shape where the grounded electrode is in the form of a conducting liquid jet;

Figure 10 is a simplified sectional view with an electric circuit diagram of a device for plasma surface treatment of the two sides of a container wall according to the invention;

Figure 11 is a view similar to that of Fig. 10 of another variant according to the invention;

Figures 12 and 13 are simplified sectional views with an electric circuit diagram of a device for the plasma treatment of inner surfaces of a plurality of containers such as bottles, the plasma being generated by electrical pulse discharges;

Figure 14 is a simplified sectional view of a plasma treatment device according to the invention where the plasma is produced by adiabatic (isentropic) compression;

Figure 15a is a simplified sectional view of a plasma treatment device according to the invention where the plasma is produced by expansion of compressed gas generating a shock wave; and

Figures 15b and 15c are simplified views of one section of the device of Figure 15a illustrating the movement of the shock waves and the creation of the plasma.

Referring to Figures 1a and 1b, a device 1 for the treatment of a surface 2 of an object to be treated 3 generally comprises a device for plasma generation 4 including a gas supply system and an electrode 5, and a holding device 6 for holding the object to be treated. The treatment device 1 may also comprise an external vibration generator 7 that can

induce the surface 2 of the object to be treated to vibrate, by means of an oscillator in direct contact with the object or via sonic (acoustic) waves without direct contact.

A plasma 8 is created on the surface 2 of object 3 by the plasma generator 4 in a gas that can be activated plasma-chemically and is directed toward the surface 2 by a duct 9 of the gas supply system, where the duct can be formed within the electrode 5.

The surface to be treated is excited so as to vibrate, that is, it undulates. The energy needed to generate the undulation of the surface to be treated can be derived from a shock wave arising in the process of plasma creation, from a shock wave created by an external generator, of from an external vibration generator 7. A shock wave causes a body to vibrate in a transitory mode at its eigenfrequencies. The vibration amplitude can be boosted by an external vibration generator adjusted so as to generate vibrations at one or several eigenfrequencies of the object to be treated. As the vibration modes of bodies are extremely complex, the optimum choice of frequencies may be determined by tests, that is, by adjusting the frequency differently for each of a certain number of samples and determining the features of surface treatment quality.

An analysis of the surface treatment process according to the invention shows that by undulating the particles of the surface to be treated one can intensify the physicochemical interaction between the plasma particles and the surface particles. By its nature and effects, this intensification resembles that accompanying an increase in temperature of the surface to be treated when in contact with the plasma, be it a vacuum plasma, an atmospheric plasma or a high-pressure plasma.

Thus, an important feature of the invention is to intensify the process of plasma-chemical interaction, be it for deposition of a film, for etching, the creation of a surface alloy, or other kinds of treatment, without a significant rise in the temperature of the object to be treated. This technical solution is very important and opens up wide

perspectives, particularly for the plasma treatment of bodies made of material that do not support a rise in temperature. It also valorizes in a new way the action of a cold plasma on a surface, i.e. the action of a plasma out of thermodynamic and chemical equilibrium (see the definition on page 27 of the book of Baddour and Timmins cited earlier). The possibility of exciting the surface to be treated by a mechanical vibration while leaving it cold allows one in fact to decisively remedy the disadvantage inherent in the use of a cold plasma on a cold surface, since the interaction between the plasma and the surface to be treated is strongly intensified.

Figures 2a and 2b present SEM (Surface Electron Microscope) photographs of the surface of an 0.5-liter-capacity PET bottle after a plasma treatment without excitation of the surface to be treated. In this case a silicon oxide film was deposited. The plasma employed in this example is a HF (high-frequency) pulse discharge plasma generated in a mixture of hexamethyldisiloxane vapors and argon. After the treatment the bottle was mechanically folded, and in these photographs one notices chips 10 and scales 11 formed on the surface. These chips and scales can fall off and become incorporated into the liquid, thus representing a hazard to the consumer. This also increases the permeability of the surface. By tests involving these bottles it could be established that the impermeability RIF (Relative Impermeability Factor) of the barrier film was about 10 for oxygen, relative to an untreated surface. In the case of Fig. 2c the same surface treatment was carried out while adding vibrations having a frequency of about 21 kHz, that is, in the ultrasonic region, with the aid of an external ultrasound generator. The temperature of the PET walls of the bottle was measured during the treatment with a thermocouple, which showed that the temperature did not rise above 45 °C. This temperature is well below the maximum temperature of PET treatment, which is about 60 to 70 °C. The bottle was then folded mechanically in the same way as the samples of Figures 2a and 2b, and one can notice in the SEM photograph that the barrier film obtained is sound and flexible, since neither chips nor scales are formed. The level of

impermeability of the barrier film is very high. According to sample measurements, the RIF is about 30 for oxygen, relative to an untreated surface.

It should be noted that the process according to the invention allows one to employ a plasma in vacuum, under atmospheric pressure, or under high pressure, since the action exerted by the vibrations of the surface to be treated on the interaction of this surface with the plasma does not significantly change with the pressure at which the plasma is generated. The treatment efficacy, on the other hand, again does not signicantly change with the manner in which the plasma is generated, be it in a continuous manner, with supply from DC sources, AC sources, high-frequency, microwaves, or pulses. In the latter case, the pulse period is preferably longer than the period of the vibration to which the object to be treated is subjected, in order to make sure that the contact between the plasma and the surface to be treated comes about.

The shock wave originating with plasma creation can be generated by isochoric heating of a volume fraction of gas that can be activated plasma-chemically, by emitting an electrical pulse discharge obeying certain parameters, directly into the process gas. The volume fraction in question heats up, its pressure rises rapidly above the critical pressure above which a shock wave forms which propagates throughout the volume of the gas mixture and is followed by a plasma formed by particles of the process gas that are heated, excited, and ionized. This procedure is above all efficient when the electric current pulses are accomplished along the surface of the body to be treated, which consists of insulating materials. It can be used to good advantage to treat a complicated surface such as the inner walls of bottles, tubes, gasoline tanks and other containers.

In Fig. 3a, a device 1 for the treatment of an inner surface 2 of an object to be treated 3, here a bottle, comprises a device for plasma generation 4 by electrical pulse discharges that is provided with a gas supply system comprising a duct 9 which can at once function as live electrode 5, a holding device 6 with an insulating element 12 for

holding the object to be treated, and a grounding electrode 15. The treatment device 1 can also include an external vibration generator 7, here an ultrasound generator, that can cause the inner surface 2 of the bottle to vibrate, a vibration sensor 13 that can be connected to a command module of the vibration generator 7, and a temperature sensor 14, for instance a thermocouple, to check the temperature of the container wall.

A plasma 8 is created inside the container 2 by current pulses flowing from the central electrode 5 that is working in the electric or autoelectronic field emission mode (as defined in the monograph of S. Krapivina, Plasmachemical processes in engineering, Chemistry Publ., Leningrad (1981), p. 27) to the grounding electrode 15. The grounding electrode 15 is arranged and shaped so that it can sustain the amplitude of the applied electric field and admit the creation of branched plasma discharges consisting of a superficial network of plasma filaments 16. The amplitude of the applied electric field must be large enough to ensure discharge initiation by breakdown.

Electrode 5 which at once functions as a duct 9 through which the process gas is introduced into the container can be inclined forming an angle α to the container's axis of symmetry, so as to favor plasma formation along its inner surface 2. A gas having a weak ionization energy is used, such as argon, in order to optimize discharge localization along the container's inner surface.

Referring to Figs 5 and 6, the branched plasma discharge is developed by a current pulse (I) having a rising flank of length t_1 so that the plasma inside the filaments of the branched discharge starts to form and heat up isochorically. The band designated as t_1 in Fig. 5 corresponds to the phase of isochoric heating of the plasma filaments. For t_1 one has the relation: $t_1 < d/a$, where d is the diameter of the filament when being created, and a is the speed of sound in the nonionized medium surrounding the filament. Typically $d \sim 1$ mm and $a \sim 3 \cdot 10^2$ m/s so that $t_1 < 3 \cdot 10^{-6}$ s.

At the end of time t_1 the pressure rise inside the filament, which depends on the features of discharge development, and particularly on the heating of the plasma supplied with energy by the current, generates a shock wave exciting and ionizing the gas around the filament. The activation is intense above all in zone 19 between plasma filament 16 on the surface to be treated 2, on account of the incident wave 17 intersecting with the wave 18 reflected from the surface to be treated. The current that is initially localized in this filament, after development of the shock waves mentioned passes mainly to the zone 19 that is restricted to the reflected wave 18 within which a cold plasma out of thermodynamic equilibrium develops which has a very good contact with the surface to be treated.

The amplitude of the energy developed by the electric current pulse is such that part of the energy of the incident shock wave is transmitted to the material of the object to be treated, via a penetrating shock wave 20 which is dissipated in the form of vibrations at eigenfrequencies of the object to be treated, which can be in the range of audible frequencies or of ultrasonic frequencies. The presence of vibrations can be checked advantageously with the aid of an acoustic sensor 13 in the treatment device. These acoustic vibrations will subject the atoms of the object to be treated to oscillations which make them depart from and return to their positions of static equilibrium, and during their departure create a situation that favors their chemical union with the particles of the medium that is ionized and activated by the plasma, for instance with silicon and oxygen atoms during deposition of a SiO_x film.

Figure 7 shows the result of recorded vibration frequencies of a PET bottle (0.5 liters) obtained during the treatment by a HF pulse discharge producing a branched jet of plasma filaments according to the invention. One sees in this example that the packets of acoustic vibrations having a relatively large amplitude have frequencies are in the regions of about 6080 Hz and 10,000 Hz.

Particularly in the ultrasonic region, acoustic vibrations applied during the surface treatment exert a catalyzing role that is similar to an increase in temperature of the object to be treated. Ultrasonic vibrations have the advantage that the object to be treated remains relatively cold as compared to treaditional plasma treatment processes, since the energy of the ultrasonic vibrations is dissipated in the volume bordering the shock wave, rather than locally. Thus, the heating of the object to be treated that results from dissipation of the waves will be relatively slight.

The current pulses should nevertheless be limited in time. The energy set free during current flow in the plasma, which at first is out of thermodynamic equilibrium, is expended on one hand for activating the carrier gas particles (for example, O_2, O, Si, maybe C, H), on the other hand for heating the object to be treated, as well as the plasma itself, which increases in volume. These last-mentioned effects constitute a certain disadvantage for the surface treatment and should be limited. In the case of film deposition, the plasma heating and volume increase favour the formation of powder which deposits on the surface to be treated, thus contaminating it, resulting for instance in poor adhesion of the film to the surface to be treated and in poor barrier quality.

Returning to Fig. 5, the band designated by t_2 in Fig. 5 corresponds to a phase of expansion of the plasma filaments. The current pulse length t_2 is so selected that the plasma remains cold and develops along the surface to be treated, and that the temperature of the object to be treated will not rise above its temperature of destruction. This can be checked by temperature measurements of the object during or immediately after its treatment with a temperature sensor, for instance a thermocouple 14 positioned close to or on the object to be treated, as shown in Fig. 3, and connected to the plasma generation device 4. In an industrial process, the sensor can be employed in the phase of startup to adjust and calibrate the plasma generation parameters, and particularly the pulse length t_2 and pulse interval t_3.

On the other hand, the current pulse length t_2 must be sufficient to activate and precipitate a maximum number of particles from the plasma-chemically activated medium onto the surface to be treated, which is verified by evaluating the actual results of the treatment on a certain number of samples.

As the plasma filaments that produce the mechanism described above are spaced relatively far apart, the pulses must be repeated in order to uniformly coat the entire surface to be treated. In order for the filaments not to return onto the sites of prior filaments when a new pulse is applied, the time interval t_3 between two pulses should be longer than the "post-discharge" plasma lifetime t_4 (as defined, for instance, in the monograph of A. Ricard, Plasmas Réactifs, SFV, 1995), and long enough so that the particles that have precipitated on the surface to be treated and have been brought in contact with the particles of the surface itself, can attain their final stable (or metastable) state that will be determining for the properties required of the surface to be treated.

For instance, during deposition of a polymer film based on the plasma precipitation of a mixture of activated C, H, and CH_y particles, the time t_3 between the plasma pulses should be such that between the plasma pulses the polymerization process can be completed on the surface to be treated. This completion is advantageously accelerated by the presence of acoustic vibrations.

For plasmas containing compounds such as O_2, N_2, H_2, Si, and C, the time lag between pulses will preferably be $t_3 \geq 1$ to 10 ms.

Advantageously, an acoustic vibration, preferably in the region of ultrasonic frequencies, that is being applied to the object to be treated, prior to the plasma treatment, offers the advantage of promoting the expulsion of foreign gases absorbed in the surface layers of the surface to be treated. Through the expulsion of these absorbed gases, it can be avoided that during local heating of the material by the plasma, a flux of these gases

would be created that opposes the flux of activated plasma particles and would prevent them from reaching the surface to be treated.

Advantageously, by applying an acoustic vibration after the plasma treatment to the object to be treated one will be able to expel the residual gases and the powder particles that might have become adsorbed during treatment on the treated surface.

The acoustic vibrations of the object to be treated which arise from the creation of a branched network of plasma filaments according to the invention can be supplemented by acoustic, and particularly ultrasonic, vibrations from an external source such as an ultrasonic vibration generator. The frequency can be selected so as to be equal to one of the eigenfrequencies of the object to be treated, which can be measured with a vibration sensor. In this case the resonance effect will substantially improve the quality of the applied treatment. Other advantageous frequencies exist at which the ultrasonic vibration of the object to be treated can be amplified, particularly the frequency a/D, where D is the diameter of the container and a is the speed of sound.

Figures 4a and 4b show photographs taken with a high-speed camera of a branched plasma discharge generated with a device such as described in relation to Figs. 3, 5, and 6. In the case illustrated, the bottle rests on a plate that is grounded and in contact with an acoustic vibration generator. The parameters for plasma creation used in these examples are:

in Figs. 4a and 4b,

$t_1 = 2\ \mu s$,

$t_2 = 300\ \mu s$,

$t_3 = 2\ \mu s$,

photographic exposure time: 0.5 ms,

vibration frequency of the external vibration generator: $f = 120$ kHz;

in Fig. 4a,

electric threshold potential $U = 15$ kV,

process gas: argon;

in Fig. 4b,

electric threshold potential $U = 10$ kV,

process gas: a mixture of hexamethyldisiloxane, oxygen, and argon.

The branched plasma filaments being created move rapidly along the surface to be treated, and vanish. Each discharge is preceded by a superficial breakdown such as represented by the voltage peak 53 in Fig. 5, which gives rise to a precursor channel. The lifetime of these branched filaments corresponds to the pulse frequency of the current source that creates them. The filament network covers large part of the surface to be treated, according to the photographs, and the filaments follow the exact shape of the surface irregularities of this surface, including the bottom.

The inventors of the present invention have realized that in traditional processes the plasma tends to become detached from the surface of the object to be treated, since the motion of the object or electrode gives rise to gas motions that perturb the plasma and particularly the air inflows brought about by the boundary layer of the container wall which tend to repel the plasma from the surface to be treated. When the plasma moves away from the surface to be treated, this diminishes or cancels the concentration gradient of the active particles on the surface to be treated, and thus prevents the surface treatment, such as deposition of a film. In the present invention, the problem is avoided by the fact that the duration of the current pulses creating the plasma in the shape of a branched filament network is selected to be rather short, so that the motion of the surface to be treated is so small relative to the spot occupied by the network that the pulse duration t_2 is smaller than the ratio (d/v) between the width (d) of a filament and the speed (v) of motion of the surface to be treated in relation to the plasma. Assuming that this speed be 1 m/s (a speed that is often realized in practice), and that the width of a filament is 1 mm, a maximum value of 10^{-3} s is obtained for t_2. The pulse duration t_2 is

actually subject to an even stricter condition, viz., the limitation imposed on the temperature of heating of the surface to be treated. The tests performed while developing this invention have shown that this requirement limits the pulse duration t_2 to a value not in excess of about $3 \cdot 10^{-4}$ s. The high-frequency photographs such as those of Figs. 4a and 4b show that during this time period, the filaments remain attached to the surface to be treated, and that no hydrodynamic effect is observed.

For an optimum scanning of the surface to be treated by the branched plasma network, such as that shown in Figs. 3a and 3b, one can move the plasma filaments further apart or closer together, in other words, vary the density of the bundle of plasma filaments, by selecting the shape and position of the grounding electrode 15. In Fig. 3a, for instance, one sees a branched bundle of low density, while in Fig. 3b one sees a bundle of plasma filaments highly concentrated on account of having placed an electrode 15' of small surface area outside, and radially disposed relative to the axis of symmetry of the bottle underneath the insulating holder 12.

For the plasma to sweep all of the container surface, one can carry out a relative motion between the grounding electrode and the object to be treated, for instance by rotating the holder 12 on which the container sits, or by rotating the live or grounding electrode while keeping the holder at rest, or also by moving a magnetic or electromagnetic field or generating a hydrodynamic effect in the process gases.

So as to simplify the device, one can advantageously achieve the plasma sweep along the surface to be treated, by moving the process gas supply nozzle, for instance by performing a rotation about the axis of axial symmetry of the bottle as shown in Figs. 3a to 3c. One can also improve the scanning by a treatment device such as shown in Fig. 3c, which has a gas supply device 5' provided with a feeding head 24 having a plurality of inclined ducts 9a, 9b, 9c forming an angle α with the axis of symmetry of the bottle, and distributed around this axis of symmetry. The ducts 25 can at the same time serve as

electrodes coupled to the plasma generation device 4. The feeding head 24 can be mounted so as to be rotating relative to the holder 12 of container 3. The device allows a plurality of branched plasma jets 8a, 8b, 8c to be generated which are distributed around the inner surface of this container. Rotating the process gas supply ducts causes the plasma to be rotated through hydrodynamic and electrostatic effects. The hydrodynamic effect on the other hand also improves the evacuation of residual gases after the treatment.

The entire surface of the container can therefore be treated, either by one or several sweeps of the plasma when the grounded electrode or the live electrode which serves at once as the process gas supply duct is moved, or by repeated pulses on the entire surface to be treated, but without motion of the latter.

An important aspect in the realization of the process is the feeding of the gas mixture to the surface to be treated. The gases that bring the molecules for deposition of a film, an impermeable film for instance, can be mixed with the gas used for plasma formation, and supplied through the ducts 9, 9a, 9b, 9c in the live electrode, they can be present in the container 3 prior to the start of surface treatment, or they can be supplied into the container by a separate source. The nozzle of the live electrode may direct the gases for film coating downstream of the forming plasma. It is important that the breakdown voltage in the gas mixture be lower than that of ambient air. For this reason the gas mixture preferably contains argon. The supply system is designed for the consecutive utilization of several gas mixtures having different compositions which will allow a barrier film to be created, for instance, in the form of several layers having different chemical compositions. The deposition of a barrier film on the inside of a bottle can advantageously be terminated with the deposition of an organic layer of the type of C_xH_y that will prevent foaming of a carbonated liquid subsequently filled into the bottle.

A critical region of the object to be treated, particularly in the case of objects having a narrow neck such as bottles or the part of the inner surface close to the open end of the container (for instance of a cylindrical plastic tube), is the inclined or receding part of the inner surface close to the neck. It is advantageous in order to ensure an efficient surface treatment of this part to have ducts 9a, 9b, 9c inclined by an angle α relative to the axis of axial symmetry of the container or at least the part close to the part of the neck 26.

In the particular case where the object to be treated is a plastic tube, it turns out to be important, for instance during a treatment by which a barrier is deposited, not to treat the end of the tube that is to be closed, since the deposited film may prevent the welding of this end after filling of the tube by a consumer good. In this case angle α will be so selected that the gas mixture fed through ducts 9, 9a, 9b, 9c will contact the wall to be treated, only below the annular surface that should not be treated. In the particular case where a bottle is treated, it is possible at the end of the operations to only coat the lower part of the bottle with a polymer layer preventing foaming of the beverage during filling, while the neck lacks this layer and hence favors foaming. This would cause the beverage to foam when poured, an effect desired in the case of beer.

By adequate selection of the angle α one can also minimize the accumulation of residual treatment products, by admitting a circulation of the gases toward the open side of the container, here the neck. One also can inject the feed gases as a coaxial cone to an axisymmetric object to be treated, so that the feed gases are uniformly distributed over all of the surface to be treated. In this case the residual gases are evacuated by a central evacuating duct along the axis of this cone.

Through the contact between the plasma and the surface to be treated by a process according to the invention, one can deposit barrier layers, for instance layers containing SiO_x which is cheap and well suited for containers intended for food, by the following

effects. First the gases absorbed in the walls of the object to be treated are desorbed by the acoustic effect of a shock wave arising with the creation of the plasma and/or coming from an external source of ultrasonic vibrations, and are thus eliminated from the wall's surface layer. The plasma might also produce a superficial etching of some atomic layers liberating chemical bonds which will react with the excited particles in the plasma, particularly certain particles such as silicon and oxygen fed with the surface treatment gas. The mechanism is not fully known, but it may be that the SiO_x molecules occupy chemical bonds at the polymer surface and function as crystallization sites for formation of a barrier layer of SiO_x on the surface to be treated.

For the creation of flexible, nonbreaking barrier films having good adhesion to the walls, it is possible through the present invention to successively deposit layers having different chemical compositions, and in particular to superimpose layers of SiO_x and CH_y nicely adhering to the substrate and to each other.

In the embodiment of Fig. 8 for treatment of the inner surface 2 of a container 3 of complex shape, the pulse discharge of plasma in the shape of a plasma filament network is formed between a live electrode 5 serving at once as a process gas duct and a grounding electrode 15 that can be moved in three dimensions by a mechanism (not shown) allowing electrode 15 to run across all of the outer surface of the container so as to pull a branched plasma filament network across all of the inner surface 2 of the container.

In the embodiment of Fig. 9, the surface treatment of a container 3 of complex shape (for instance a gasoline tank) is carried out as follows. A live electrode 5 supplied by a current source 4 is situated on the outside of an enclosure 27 of the device. The container 3 is placed inside the enclosure 27, which is made of insulating material and ventilated by a flow of air or other gas 28. Two ducts 29, 30 are used to bring the gas

mixture into the tank 3 and to evacuate the residual gases from the tank, respectively. The tank can be moved and rotated through a mechanism holding the tank (not shown).

The grounded electrode can have the form of an electrically conducting liquid jet 31 coming from an injector 32 supplied by a pump 33. The electrically conducting liquid 34 collecting on the bottom 35 of the enclosure is continuously recirculated into the system of the grounded electrode. The discharge between said electrodes develops in the form of a branched plasma filament network 8.

In the embodiments of Figs. 10 and 11, two solutions for the simultaneous treatment of two sides 2s, 2b of the wall of a container 3 made of insulating material are shown.

In the embodiment of Fig. 10, discharges are produced so that the branched plasma filament networks 8a and 8b are formed in an alternating way to both sides of the wall while the two electrodes 5a, 5b are connected to opposite poles of the electrical circuit 54 of the plasma generation device 4. The container is placed on a holder 6 made of insulating material that can be rotated.

In the embodiment of Fig. 11, the electrical arrangement proposed allows the discharges to be carried out in the form of branched plasma filament networks 8a, 8b supplied in parallel. The tank 3 is in this case placed on a holder 12, and the two discharges make use of one grounded electrode 15.

In these two embodiments, live electrodes 5a, 5b serve as gas ducts. The gas mixtures sustaining the discharges may differ between the two sides of the container wall so that deposits having different compositions and properties might be formed.

The process claimed can be put to practice with equipment consisting essentially of two conveyors feeding and withdrawing the objects to be treated, and a rotating circular tray

at the periphery from where the objects to be treated are moved, each provided with a system of distribution of the gas mixtures, a current source, appropriate devices for measurements and checks, and one or more sources of acoustic vibrations, particularly ultrasonic vibrations, ensuring realization of the process. The sources of acoustic vibrations may be mounted onto the container bottom holders, so as to enhance the efficiency of the treatment on the container bottom surface. The current sources can be arranged to serve groups of objects to be treated.

During its treatment, each of the objects to be treated could be subjected to air cooling by forced convection to the object's untreated wall, for instance to the side not treated, when dealing with a container being treated.

In one mode of realization of the invention the objects to be treated could be immersed into a liquid through which they would be subjected to the uniform action of acoustic vibrations, and particularly of ultrasonic vibrations, over their entire surface. This could for instance be bottles or other containers partially immersed into the liquid bath, with the necks remaining outside, so that the liquid would be in contact with the container's outer surface, which has the advantage that the container walls can be cooled very efficiently and the plasma applied for a longer time. On the other hand, when an external source of vibrations is employed, the liquid allows these vibrations to be more uniformly distributed over the container walls, and thus to produce more uniform vibrations on the container's inner surface to be treated.

For simpler electrical connections to the treatment device, this device can be provided with a system of capacitors through which the high-frequency (HF) electrical energy is transmitted to the live electrodes without the need for a direct contact.

In the deposition of films on containers consisting of transparent, amorphous material, the treatment device may advantageously include a system of laser beams for quality

control of the film deposited. Such a system will record, either the number of photons emitted by non-linear effects while the laser beam passes through said film or the decrease of the flux of primary photons caused by their recombination as a result of non-linear effects.

In an etching treatment carried out by plasma at an object such as a single-crystal silicon wafer onto which a microelectronic structure partly protected by masks consisting of photoresist material is deposited, one can advantageously apply a undulation to the object to be treated, in a particular direction such as perpendicularly to the wafer surface, so as to produce an anisotropic etching. The degree of anisotropy will depend on the amplitude and frequency of the undulation imposed upon the surface to be treated.

When the object to be treated is a metal sheet, a plastic foil, or a textile sheet, then this object can be subjected to the simultaneous action of a plasma flux scanning the surface of this object and of a vibrating motion of the object which will intensify the cleaning, degreasing, etching treatment or film deposition caused by the plasma flux.

A similar and equally efficient realization is feasible when the object to be treated is a metallic wire, textile fibre, or polymer filament.

Another embodiment of the present invention consists in generating the plasma simultaneously in two spots on the surface of an asymmetrically shaped object to be treated, for instance a container of large volume and complicated configuration, where two high-frequency discharges in the form of branched plasma filament networks are produced between two capacitive electrodes provided with a scanning motion along the outer surface of the object to be treated.

Another mode of plasma generation of interest consists in generating plasma by adiabatic (isentropic) compression. A device for treatment by generation of such a plasma is shown in Fig. 14.

The treatment device 1 includes an enclosure 36 comprising a section that is the chamber of piston 37 and a section containing the seats for the objects to be treated 38, a solid piston 39, a gas compression device 40 provided with means for rapid expansion, an acoustic vibration generator 7, an entry duct for the process gas with valve 41, and a duct for gas evacuation with valve 42. The section with the seats for the objects 38 comprises a portion of side wall 43, a portion of bottom wall 44 fixed to the portion of side wall via a vacuum seal and vibration damping device 45. Piston 39 is mounted so as to slide inside the piston chamber 37 of enclosure 36, while the section of the chamber above the piston can rapidly be filled by high-pressure gas generated by the gas compression device 40 that is connected to this section of the chamber by a duct 46. An exit duct 47 with valve 48 allows the gases to be evacuated from the section of the enclosure above the piston when the piston 39 is lifted back up. The entry and exit duct 41, 42 allows the section with the seats of the objects to be filled with process gas, to evacuate the gas after treatment, and to fill it again with process gas.

When the piston is at the upper dead center, then the interior of the enclosure is first evacuated by a vacuum pump (not shown) connected to exit 42, then filled with a process gas supplied by the entry duct 41. The compression device 40 includes a compressed-air reservoir connected via an actuating valve with the section of the enclosure above the piston. The piston 39 is pushed downward by the compressed air and only stops when at the lower dead center 50.

The dimensions (diameter and height) of the enclosure, the initial process gas pressure, and the pressure exerted on the piston are so calculated that during its motion from the

upper dead center 49 to the lower dead center 50, the piston compresses the process gas along the adiabatic curve of Hugogniot.

The plasma is generated by adiabatic compression. It pushes the piston back, the piston returning to its upper dead center 49 while the gas above the piston is evacuated during its up-stroke via the duct 47. This embodiment has the advantage that the plasma is generated uniformly throughout the treatment space, so that the treatment will be carried out in a uniform way on all sides of the objects to be treated which are present in the enclosure.

The dynamics of the compression process is calculated so that a plasma having given parameters is formed in the treatment zone of the enclosure, and that vibrations are generated by the external source of vibrations 7 operating preferably at one of the eigenfrequencies of the objects to be treated, or at a multiple of one of the eigenfrequencies.

Another mode of plasma generation that may also be of practical interest is the generation of plasma by a shock wave. A device allowing such a plasma to be generated is schematically illustrated in Figs. 15a to 15c.

The treatment device 1 according to Fig. 15a comprises an enclosure 36 with a first section 37 holding compressed gas that is connected via a duct 46 with a valve to a gas compression device 40, and a section housing the objects to be treated 38, with a process gas entry duct 41 provided with a valve and a process gas evacuation duct 42 provided with a valve. The section housing the objects to be treated comprises a portion of side wall 43 and a bottom portion 44 which are joined via a vacuum seal acting as vibration absorber 45. The device further comprises an external ultrasonic vibration generator 7 arranged underneath the bottom portion 44. A removable separating wall 51

can be arranged so as to hermetically separate the section holding the compressed gas 37 from the section housing the objects to be treated 38.

At the start of the treatment process a vacuum pump connected to the evacuating duct 42 empties the section 38 of the enclosure which subsequently is filled with a process gas supplied by the entry duct 41. The compression device 40 compresses a process gas in the section holding the compressed gas 37. Finally the removable wall 51 is abruptly lifted in order to connect the two enclosure sections 37, 38.

The dimensions (diameter and height) of the enclosure, the initial pressure of the process gas, the position of the separating wall, the pressure of the compression gas, and other parameters are so calculated that the process gas compression behind the shock wave occurs according to the adiabatic curve of Poisson. The dynamics of the compression process produced by the incident and reflected shock wave is calculated in such a way that a plasma of given parameters is formed in the zone of the object to be treated. The object 3 is subjected to the plasma-chemical action of the plasma created behind the reflected shock wave 52', the plasma resulting from the twofold compression by the incident wave 52 and the reflected wave 52'. Part of the energy of the incident shock wave 52 is absorbed by the object to be treated 3, in the form of a shock wave 52" propagating inside the object at the speed of sound, which is rather higher that the speed of sound in the plasma. The wave inside the object is reflected at the opposite wall 26, and thus performs a forth-and-back motion becoming dissipated in the form of acoustic vibrations.

These vibrations of the surface of the object to be treated provoke an intensification of the plasma-chemical reactions between the plasma and the particles of the surface to be treated 2a. One can boost the amplitude of the vibrations by an external source of vibrations 7 emitting for instance a frequency close to or identical with one of the eigenfrequencies of the object or a multiple of this frequency.

However, the frequency of this external vibration can be selected so as to correspond, neither to the vibration frequency of the shock wave in the object to be treated nor to an eigenfrequency of the object to be treated.

Nonlimiting examples of realization of the process according to the invention are given hereafter.

Example 1

Deposition of a silicon oxide film on the inner surface of a single-layer PET bottle (0.5 liters) by the HF method

Base products used consecutively and repetitively: Ar, O_2, HDMS, CH_4

Maximum voltage of the current source: 21 kV

Discharge current amplitude: 10 A

$t_1 = 3\ \mu s$

$t_2 = 300\ \mu s$

$t_3 = 40$ ms

Duration of treatment: 30 s

Major barrier material: SiO_x (x = 1.96)

Barrier thickness: 180 - 190 Å

Height of barrier for oxygen (volume of oxygen diffusing across the bottle wall per day):

prior to treatment:	0.06 cm^3/bottle·day
after treatment:	0.0001 cm^3/bottle·day

Relative barrier coefficient for oxygen: RIF* ~ 60

Barrier coefficient for CO_2: RIF* ~ 15

*) RIF = Relative Improvement Factor

Example 2

Deposition of a silicon oxide film on a single-layer polyethylene tube (200 ml)

Base products used consecutively: Ar, O_2, HDMS, TEOS, CH_4

Maximum voltage of the current source: 10 kV

Discharge current amplitude: 8 A

$t_1 = 2$ µs

$t_2 = 200$ µs

$t_3 = 10$ ms

Duration of treatment: 30 s

Major barrier material: SiO_x (x = 1.95)

Barrier thickness: 250 Å

Height of barrier for oxygen:

prior to inside treatment:	0.7 cm^3/tube·day
after inside treatment:	0.005 cm^3/tube·day
after outside treatment:	0.1 cm^3/tube·day
after treatment on both sides:	0.002 cm^3/tube·day

Barrier coefficient for oxygen:

after inside treatment: RIF ~ 140

after outside treatment: RIF ~ 7

after treatment on both sides: RIF ~ 350.